

New Ground State of Relaxor Ferroelectric $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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High energy x-ray diffraction measurements on $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) single crystals show that the system does not have a rhombohedral symmetry at room temperature as previously believed. The new phase (X) in the bulk of the crystal gives Bragg peaks similar to that of a nearly cubic lattice with a slight tetragonal distortion. The Bragg profile remains sharp with no evidence of size broadening due to the polar micro crystals (MC). However, in our preliminary studies of the skin, we have found the expected rhombohedral (R) phase as a surface state. On the other hand, studies on an electric-field poled PZN single crystal clearly indicate a rhombohedral phase at room temperature.

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I. INTRODUCTION

Relaxor ferroelectric materials with extremely high piezoelectric responses are of great interest to both the scientific and industrial communities¹. Among those the lead perovskite system $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PZN-xPT) has been studied extensively, due to its extraordinary piezoelectric properties near the morphotropic phase boundary (MPB)^{2,3,4,5,6} (see Inset of Fig. 1). For PZN-xPT, the piezoelectric response reaches maximum at $x = 8\%$, which is located on the rhombohedral (R) side of the MPB¹. As shown in Fig. 1, the pure PZN system has been reported to undergo a cubic (C) to rhombohedral (R) phase transition at $T_C = 410\text{ K}$ ³. In the lower portion of Fig. 1, a schematic of the rhombohedral angle α vs temperature is shown⁷.

The properties of relaxor ferroelectrics have been most commonly described in terms of the formation of polar nanoregions (PNR)^{8,9}. It was found that in relaxor ferroelectric systems, PNR start to form at the Burns temperature¹⁰ and persist below T_C . Neutron diffuse scattering measurements^{11,12} have provided direct evidence on the existence of PNR. In pure PZN, diffuse scattering intensity due to local atomic shifts starts to appear at 450 K and keeps growing when the temperature reaches below $T_C = 410\text{ K}$ ¹¹ (see Fig. 1 for a schematic of the neutron diffuse scattering intensity vs temperature). It was widely accepted that these PNR create random fields under zero external fields and form ferroelectric micro crystals (MC), which leads to local rhombohedral symmetry.

The structures of PZN-xPT single crystals have been studied before, but only with electric field pre-poled crystals. Measurements with electric field along the crystallographic (111) direction¹³ confirm a rhombohedral phase at room temperature in the pre-poled system. Nevertheless, no structural study of unpoled PZN single crystals has been reported in the last twenty years to our knowledge. Only until recently, Lebon *et al.* studied the single crystal of unpoled PZN using x-ray diffraction⁷ with Cu

K_β x-ray (8.9 keV), and observed the rhombohedral splitting for temperature below T_C as previously believed.

Recently, Ohwada *et al.* performed neutron diffraction measurements on the $x = 8\%$ PZN-xPT system¹⁴ in order to study phase transitions in the system with both field-cooling (FC) and zero-field-cooling (ZFC). Surprisingly, they did not obtain the rhombohedral (R) phase during the zero-field cooling process, but discovered a new, unidentified phase (X). This new phase differs from the rhombohedral phase by having nearly cubic lattice with a slightly different c -axis. It is therefore interesting to further investigate the ground state of unpoled PZN single crystal at room temperature to obtain the real crystal structure.

In our preliminary measurements with 32 keV x-rays on unpoled PZN single crystals, rhombohedral splittings similar to that obtained in Lebon's paper was also observed for peak (111) at room temperature. However, the bulk property probed by high energy x-ray (67 keV) at room temperature show a very different structure which is not the widely believed rhombohedral phase. Instead, the new ground state is an unidentified phase, which has a nearly cubic lattice with small tetragonal distortions, and closely resembles phase X found in the $x = 8\%$ system. We believe that measurements performed at lower x-ray energies only show the properties of the system near its surface. We will discuss this surface phase shortly below, but the main purpose of this paper is to describe the new phase X discovered in the bulk of the crystal.

II. EXPERIMENT

Single crystals of PZN were grown by spontaneous nucleation from high temperature solution using PbO as flux, as described in Ref. 15. Two crystal plates of triangular shape (with 3 mm edges and 1 mm thick) were cut with large surfaces parallel to (111) cubic plane from one and the same as-grown bulk crystal. The (111) cubic

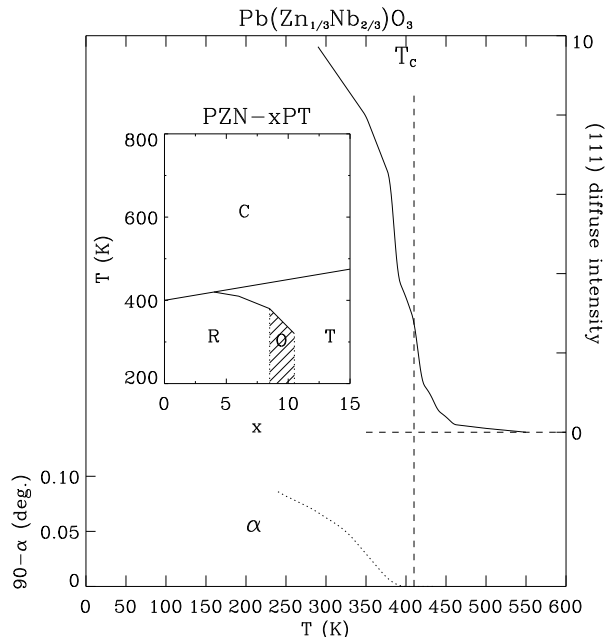


FIG. 1: Structural properties of PZN. The dotted line in the lower left shows the a schematic of the rhombohedral angle α vs temperature obtained by Lebon *et al.*⁷; the solid line in the upper right corner shows intensities of neutron diffuse scattering (Ref. 11). The inset shows the recently published phase diagram in the vicinity of the MPB (Ref. 5).

faces of both samples were mirror polished using a series of diamond pastes down to 3 μm . The (111) cubic faces of one sample were sputtered with gold layers. Two gold wires were attached to one corner as electrodes using silver paste. It was then heated to about 200 C (above TC), poled by applying an electric field of 20 kV/cm and cooled down to room temperature with the field kept on. The other sample was not poled or thermally treated, therefore a larger mechanical strain may remain in the crystal.

Previous experiments by Noheda *et al.*^{16,17} show that x-ray diffraction results on PZN-xPT single crystals have a strong dependence on the surface structures. It is therefore important to use a high energy x-ray beam preferable in transmission (Laue) mode in order to probe the bulk property of the crystal. Our primary measurements were performed using 67 keV x-rays at X17B1 beamline of the National Synchrotron Light Source (NSLS). The beamline is equipped with a super-conducting wiggler source (4.2 Tesla) providing a synchrotron x-ray beam with a critical energy of 22 keV. A monochromatic x-ray beam of 67 keV, with an energy-resolution of 10^{-4} ($\Delta E/E$), was produced by a sagittal-focusing double-crystal monochromator using silicon [311] reflection with both crystals in asymmetric Laue mode¹⁸. The energy of the incident beam was calibrated by 4- θ method using a strain-free float-zone silicon crystal. A perfect-crystal silicon analyzer was used with the symmetric Laue reflection

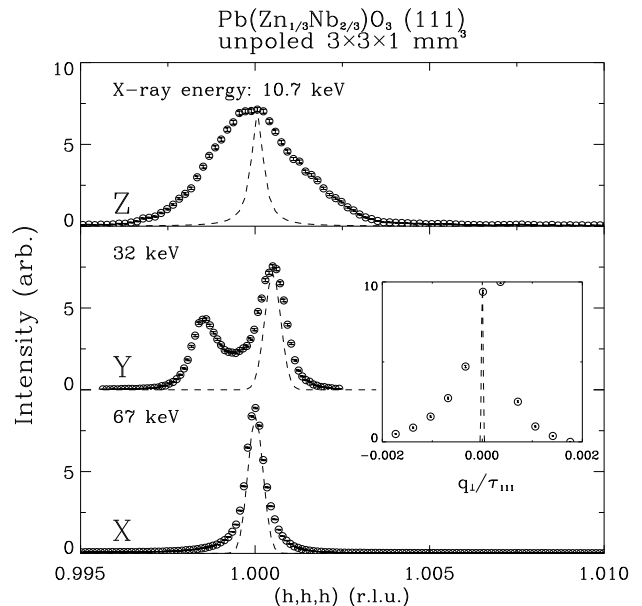


FIG. 2: Longitudinal scans (θ - 2θ scans) of (111) reflection on the unpoled PZN single crystal using different x-ray incident energies. The inset is a transverse scan of (111) taken at x-ray energy of 67 keV. Units of the horizontal axis are multiples of the pseudocubic reciprocal lattice vector (111) $|\tau_{111}| = \sqrt{3} \cdot 2\pi/a_0$.

[220]. The focused beam on the sample was 0.5 mm by 0.5 mm, with a horizontal and vertical divergence of 50 and 10 micro-radians, respectively. The diffraction plane for the sample and analyzer was in the vertical plane. For comparison, as discussed later, we also performed x-ray diffraction measurements on beam line X-22A at the NSLS with lower incident photon energies (32 keV and 10.7 keV).

III. SKIN EFFECT

In Fig. 2 we show longitudinal scans along the pseudocubic (111) direction of the unpoled PZN single crystal with different x-ray energies. The instrument resolution curves measured using the (111) reflection of a perfect Ge crystal are plotted as dashed lines in the figure. The x-ray penetration length and lattice parameters extracted from the data are listed in Table I.

For x-ray energy of 10.7 keV, the scan shows a broad peak along (111) direction. This can be a result of a collection of micro crystal domains contributing to the total diffraction intensity. The full width at half maximum (FWHM) of the broad peak is $2\Gamma = 0.0084 \text{ \AA}^{-1}$, corresponding to an the average size of the micro crystal domains of $L = 0.94\pi/\Gamma \approx 700 \text{ \AA}$ ¹⁹. When probed with 32 keV x-rays, the pseudocubic (111) reflection splits into two peaks. Both peaks have widths slightly larger than

the resolution width. If this splitting is related to a rhombohedral distortion, and the two peaks are indeed the (111) and $(\bar{1}\bar{1}\bar{1})$ reflections from different domains, the rhombohedral angle α can be determined from the positions of the two peaks (Table I). The result ($\alpha = 89.916^\circ$) is in agreement with previous measurements (Fig. 1). Yet the scan with 67 keV shows only one sharp, resolution-limited peak at (111). No rhombohedral splitting was observed. Also line broadening due to finite (micro) crystal size effect diminishes at 67 keV.

Lattice parameters of the different phases, marked as X, Y, and Z in Fig. 2, can be determined by assuming cubic lattice for phase X and Z, and rhombohedral lattice for phase Y (Table I). The inconsistency between data sets taken at different x-ray energies indicates that the skin effect plays an important role in our measurements. Our diffraction measurements with lower energy x-rays were all performed in a reflection mode, because the low energy x-rays were not able to penetrate the 1-mm thick sample; but with 67 keV x-rays, all the measurements were taken in the transmission mode where the x-ray beams were going through the bulk of the sample. At 67 keV, the x-ray penetration length is an order of magnitude larger than that at 10.7 and 32 keV, and is therefore probing more deeply into the bulk of the crystal. Among the different phases observed, the Y and Z phases are more surface structure related. They have distinct features due to inhomogeneities and the microscopic strain caused by boundary conditions near the crystal surface. The X phase, on the other hand, describes the bulk structure of the system at room temperature.

TABLE I: $\{111\}$ reflection of unpoled PZN crystal measured at different x-ray energies.

x-ray energy (keV)	10.7	32	67
Penetration depth (μm)	13	59	412
d-spacing d_{111} (\AA)	2.3530	2.3462	2.3514
d-spacing $d_{\bar{1}\bar{1}\bar{1}}$ (\AA)	-	2.3416	-
a (\AA)	4.0755	4.0578	4.0728
α (deg.)	-	89.916	-

IV. BULK PROPERTIES - PHASE X

67 keV x-ray diffraction results from the poled PZN single crystal are shown in the top panel of Fig. 3. Mesh scans in reciprocal space around the pseudocubic (111) and $(\bar{1}\bar{1}\bar{1})$ reflections were performed, by doing a series of θ scans at a set of 2θ values around the pseudocubic $\{111\}$ reflections. As expected for a rhombohedral structure, (111) and $(\bar{1}\bar{1}\bar{1})$ reflections occur at different 2θ s, i.e. d_{111} and $d_{\bar{1}\bar{1}\bar{1}}$ are different due to the rhombohedral distortion. Based on the positions of (111) and $(\bar{1}\bar{1}\bar{1})$ reflections, the rhombohedral lattice parameters can be obtained: $a = 4.0608 \text{ \AA}$, and $\alpha = 89.935^\circ$. Weak (111) peak is likely due to a small part of the skin which is

not fully poled. The position of the weak peak in the (111) mesh does not match exactly with that of the $(\bar{1}\bar{1}\bar{1})$ peak shown in the other mesh scan. Based on this splitting in the (111) scan, one can extract a different set of rhombohedral lattice parameters: $a = 4.0551 \text{ \AA}$, and $\alpha = 89.901^\circ$. The likely cause of this discrepancy is the skin effect of imperfect poling near the crystal surface.

Results from the unpoled PZN single crystal are, however, entirely different. In the lower panel of Fig. 3, we show four mesh scans at the pseudocubic (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, and $(\bar{1}\bar{1}\bar{1})$ reflections for the unpoled PZN single crystal, using high energy (67 keV) x-rays. The peak intensities, positions and widths are almost identical in all four scans. The lack of diffraction geometry dependence confirms that it is the bulk structure, instead of the surface states, that was being probed with the 67 keV x-ray beams. Analysis of the data show that all four $\{111\}$ reflections have similar d-spacings within 0.05% (Table II). The four $\{111\}$ mesh scans provide the key evidence that the structure of the unpoled PZN single crystal is not rhombohedral as previously believed. To further identify this phase, we performed similar mesh scans at the pseudocubic (100), (010), and (001) reflections. Our results (Table II) show that the c -axis is about 0.1% longer than the a - and b -axes. However, we did not observe any peak splitting at the $\{100\}$ reflections corresponding to the tetragonal distortion. This suggests a tetragonal (T) type distortion but the true symmetry can only be determined by detailed measurements and analysis of Bragg peak intensities. The small tetragonal distortion may be due to the remaining mechanical stress caused by polishing of the sample. In this paper we refer to this new unidentified phase of PZN as phase X.

TABLE II: 67 keV x-ray diffraction results on unpoled PZN crystal (with 0.05% uncertainty).

Reflection	2θ (deg)	$\delta(2\theta)$ (deg)	d (\AA)
111	4.5086	0.0024	2.3514
$\bar{1}\bar{1}\bar{1}$	4.5081	0.0022	2.3516
$\bar{1}\bar{1}\bar{1}$	4.5072	0.0035	2.3521
$\bar{1}\bar{1}\bar{1}$	4.5062	0.0025	2.3526
100	2.6009	0.0020	4.0754
010	2.6011	0.0016	4.0750
001	2.5975	0.0016	4.0801

Our results suggest that the ground state of PZN, namely the phase X, be nearly cubic with a slight tetragonal distortion of 1.001, characterized by its lattice constants shown in Table II. However, the true symmetry of this phase is not fully known yet. For this purpose, it is essential to study the changes of Bragg intensities through T_C of 410 K. It is known that the (200) peak shows a large increase through T_C , and it is interpreted as the reduction of extinction effect by the formation of micro ferroelectric state below T_C . This is consistent with the large mosaic observed (see Inset of Fig. 2) in our measurements despite of the sharp longitudinal width. We

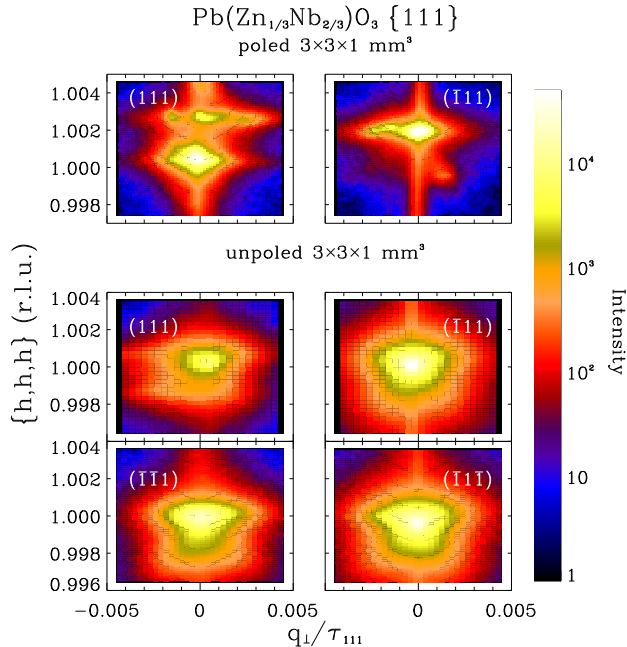


FIG. 3: Mesh scans taken around pseudocubic $\{111\}$ positions of the poled (top frame) and unpoled (bottom frame) PZN single crystals. The x-ray energy is 67 keV. The intensity is plotted in log scale as shown by the scale bar on the right side. Units of axes are multiples of the pseudocubic reciprocal lattice vector (111) $|\tau_{111}| = \sqrt{3} \cdot 2\pi/a_0$.

plan to carry out more detailed studies on Bragg line widths, intensities, as well as lattice constants on the unpoled PZN crystal at temperatures through T_C .

V. DISCUSSION

The big puzzle at present is why such a sharp Bragg profile is observed below T_C where it has already been demonstrated that a large volume of the crystal is occupied by the PNR as indicated by the increasing diffuse intensities through T_C (see Inset of Fig. 1). We can visualize a scenario describing our results: as shown in Fig 1, polar nano regions exist in the crystal with spontaneous polarizations below T_C , but they are incapable of merging and forming ferroelectric micro crystals (MC) with rhombohedral symmetry as previously expected; and the whole system still retain in average a nearly cubic lattice. The average nearly cubic lattice gives strong and sharp Bragg peaks at the pseudocubic reflections. When an electric field is applied to the crystal during the cooling process, the PNR align with the external field, thus making the overall system symmetry rhombohedral instead. The important question in this scenario is what is preventing the PNR from forming ferroelectric micro crystals. Recently Hirota *et al.*¹² demonstrated that a uniform displacement of the PNR along their polar direction relative to the surrounding unpolarized cubic matrix is

required. This phase shifted condense mode properly reconciles the neutron diffuse scattering intensities as well as the soft TO phonon intensities in another prototypical lead perovskite relaxor system $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN)²⁰. We believe that this uniform phase shift may be playing a key role in answering the previously raised question. When the PNR are shifted with respect to their surrounding environments, the lattice distortion could cause a higher energy barrier for the PNR to reorient, therefore “freezing” the PNR at their local polarizations; and makes it harder for them to merge into larger polar crystals which eventually lead to a long range ferroelectric phase below T_C .

It is also important to realize that in the other relaxor system PMN, similar behavior has been observed below T_C . It was also found that with zero electric field cooling, PMN undergoes a transition into a random-bond-driven glassy state instead of a ferroelectric state²¹. This system has been intensively investigated in recent years^{22,23}, and a more detailed description on this compound can be found in the review article by Ye²⁰. Until recently the accepted picture was that PMN remain cubic through its apparent T_C of 220 K. The recent neutron scattering paper by Wakimoto *et al.*²⁴ has changed the picture. The soft mode energy square increases linearly with temperature below T_C , as expected for ordered ferroelectric phase. Our discovery of phase X in PZN hints that the “cubic” phase of PMN below T_C might be the phase X. Further experiments are needed to confirm this speculation as well as the phase X in the rhombohedral region of PMN-xPZ²⁵.

VI. CONCLUSIONS

In summary, we have performed detailed high energy x-ray diffraction measurements on single crystals of the relaxor ferroelectric PZN. A new phase (X) was discovered at room temperature having nearly cubic lattice with a slight tetragonal distortion. At temperature below T_C , the system does not transform into a long range ferroelectric phase. Instead, the system is best described by a collection of local polar nanoregions embedded in an overall nearly cubic lattice. The PNR do not merge into large polar domains with long range ferroelectric order. The discovery of phase X in both pure PZN and 8% PZN-PT¹⁴ indicates that the ground state of the previously believed rhombohedral (R) side of the MPB need to be modified. We also believe that a similar phase exists in the other prototypical lead perovskite relaxor ferroelectric PMN as well. This disordered ground state would change the whole picture of the phase diagram of the relaxor system, and provide new exciting challenges for future theoretical and experimental work. In addition, our preliminary studies on the skin effect of the crystal show very interesting results. Different profiles (Y and Z) have been observed from the surface of the crystal under different conditions. These surface states are very

important but not fully understood yet. Further studies are being carried out to better identify these surface states and their origins.

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